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WITNESS my hand this Fourteenth day of January 2004

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SUPPORT AND SALES

REMOVING CONTAMINANTS FROM SULFIDIC MATERIALS

Field of the Invention

The present invention relates to a method for removing a contaminant from a sulfidic material. The present invention has been developed primarily for removing environmentally hazardous contaminants such as arsenic, antimony and bismuth from sulfidic materials such 10 as pyritic ores, especially where such ores have a high carbon content, and the invention will be described partly with reference to this application. In addition, in certain applications, the present invention allows for the recovery of precious metals such as gold, silver etc where 15 such metals are present in the pyritic ore. However, it should be appreciated that the invention has broad application to a wide variety of sulfidic ores, not only for metal recovery, but also in processing waste materials and residues for subsequent disposal.

Background to the Invention

Across the world there are significant deposits and quantities of sulfidic materials including economically desirable metals to recover, especially precious metals such as gold and silver. For example, there are significant deposits and stockpiles of pyritic ores including gold and/or silver and other precious metals, however a number of these deposits are contaminated with difficult to process contaminants such as arsenic, and antimony, bismuth or other heavy metals.

Where a sulfidic material includes a contaminant such as arsenic, the use of conventional smelting or roasting techniques to treat the material for metal recovery result in the formation of arsenic trioxide which is difficult to collect and highly toxic if released to the environment. Where the sulfidic material also has high carbon content, smelting or roasting can produce high levels of carbon

lioxide (green house gas)

US6461577 discloses a process for treating sulfidic materials containing arsenic where the sulfidic material is subjected to a two-stage bio-leaching process to

5 solubilise the arsenic. The split configuration of the leaching process necessarily introduces process complexity, as does the use of bio-leaching bacteria.

It would be advantageous if an alternative hydrometallurgical process could be provided for treating 10 contaminated sulfidic ores and concentrates, with the attendant advantages of hydrometallurgical processing (including process simplicity, absence of emissions, lower energy requirements etc.).

15 Summary of the Invention

In a first aspect the present invention provides a method of removing a contaminant from a sulfidic material comprising the steps of:

•mixing the material in an aqueous solution wherein a multi-valent species of a relatively high oxidation state oxidises the contaminant to render it soluble in the solution, produces a contaminant refined material, and is reduced to a relatively lower oxidation state; and precipitating the contaminant from the solution whilst regenerating the multi-valent species to its relatively high oxidation state.

Advantageously, by precipitating the contaminant whilst regenerating the multi-valent species, the method can be operated in a closed loop or recycle mode with the attendant economic benefits (ie. simplicity, low energy consumption, preservation of mass balance etc.). The inventors have also observed that the method can be applied to difficult to treat ores and concentrates including assenopyrites, especially those having a high carbon content.

Preferably the multi-valent species oxidises the contaminant in a leaching stage, and preferably the

Contaminant is precipitated from the solution in a precipitation stage through the introduction of an oxidant which simultaneously causes the multi-valent species to be exidised to its relatively high exidation state.

5 Typically the leaching and precipitation stages are separated, although they may be combined in a single operating stage, or be conducted in a combined multi-stage operation. In this regard, the leaching process may be a single stage or multi-stage process and, when multi-stage, is typically operated counter-currently:

Preferably, after precipitating and removing the contaminant and regenerating the multi-valent species to its relatively high exidation state, the solution is recycled to the leaching stage. Recycling the solution to the leaching stage is desirable for overall process economics and is advantageous because the multi-valent species is regenerated to its original (pre-leaching) exidation state.

Preferably, in the precipitation stage, the solution ph is adjusted to and maintained at around ph 2-3. This may require the addition of an alkali agent, for example, an alkali salt such as calcium carbonate, calcium oxide, sodium carbonate, sodium bicarbonate etc. Typically in the precipitation stage the oxidant which causes contaminant precipitation and oxidises the multi-valent species is air, oxygen, chlorine gas, hydrogen peroxide etc. In pyritic ores the contaminant typically precipitates as iron/contaminant-oxidate form (eg iron arsenate).

Preferably after contaminant precipitation, solution
30 Eh and ph are restored to their levels for contaminant
leaching, to enable solution recycle to the leaching
stage. This can be achieved by eg. regulating the addition
of oxidant after contaminant precipitation.

In a typical application of the present invention, the sulfidic material includes, in addition to the contaminant, a metal to be recovered. In this regard, the method preferably further comprises a metal recovery stage

which is provided intermediate to contaminant oxidation and contaminant precipitation. Typically the metal to be

recovered is a precious metal such as gold, silver,

platinum and other platinum group metals, the recovery

However, other economically significant metals may

alternatively or additionally be recovered including

copper, nickel, zinc, lead etc. In addition, in certain

applications the contaminant may itself be desirable to

10 recover. For example, the contaminant may be economically valuable, prompting its recovery from the contaminant

precipitate (eg. this may occur in the case of antimony,

bismuth, cadmium etc.). When the contaminant constitutes

the metal to be recovered, the metal recovery stage can 15 additionally or alternatively be provided after

contaminant precipitation.

Typically, however, metal-recovery is conducted in line and preferably involves adsorption of the metal onto carbon in a carbon column, typically activated carbon. 20 Alternatively, other metal recovery processes may be

employed including ion exchange, solvent exchange, etc.

Preferably, prior to metal recovery and after contaminant oxidation, the method further comprises a material separation stage to remove the refined material

from solution. In this regard, preferably the solution is ··· 25. subjected to a thickening stage; after contaminant oxidation and prior to the material separation stage; to thicken the refined material and render it easier to separate from the solution. Preferably, separation from

.30 the solution involves filtering the refined material from the solution, however other separation methodologies may be employed such as solid/liquid settling, solution evaporation, centrifugation etc

The separated refined material can then be subjected 35 to further material treatment to recover any metal remaining therein. In this regard, because the contaminant has been removed, either entirely or

substantially, from the sulfidic material, the material may now be subjected to a conventional smelting or reasting process, and optionally to cyanide leaching, to recover any remaining metal therein (for example, where the metal is a precious metal such as gold).

After the contaminant precipitation stage, preferably the method further comprises a contaminant separation stage to remove the contaminant from solution prior to further metal recovery, or prior to recycling the solution

10 to the material mixing (leaching) stage. In this regard, a thickening stage is preferably employed, after contaminant precipitation and prior to the contaminant separation stage, to thicken the contaminant and to render it easier to separate. Typically the contaminant 15 separation is facilitated by filtration, but other separation methodologies may be employed.

Preferably the contaminant is oxidised in a highly acidic aqueous solution typically of pH less than 1. In this regard the solution pH is typically controlled by adding thereto an acid such as sulfuric acid, hydrochloric acid or any other acid which does not interfere with the process chemistry. However, the addition of an acid may not be required (eg. where sulfur present in the ore or concentrate is oxidised to generate sulfuric etc acid in the solution).

Optionally, an oxidant such as air, oxygen, chlorine gas, hydrogen peroxide, etc. can also be added during the contaminant oxidation (leaching) step, particularly where the ore concentrate is difficult to oxidise (eg. an arsenopyritic ore or concentrate of refractory nature). However, it should be appreciated that the addition of an oxidant at this stage is entirely optional and dependant on process conditions.

Preferably the solution employed throughout the 35 leaching and precipitation stages (which is typically recycled in the overall process) is a dissolved metal chloride solution, typically having a chloride

concentration of approximately 7 moles per litre. The method is preferably operated such that the metal in the dissolved metal chloride solution functions as the multivalent species (however a multi-valent species may be

separately added to the leaching process solution). In this regard, typically the metal in the metal chloride is copper (but may also be eg. iron). The multi-valent species effectively acts as an electron transfer agent. For example, in the relatively high oxidation state, the

metal may be Cu(II) or Fe(III) and in the lower oxidation state the metal is then Cu(I) or Fe (II). However, other multi-valent species may be employed including possibly cobalt, manganese and vanadium.

As stated above, typically the sulfidic material is a pyritic ore or concentrate, and typically the contaminant is arsenic, antimony, bismuth, mercury, cadmium, which occur naturally in many as-mined sulfidic materials.

In a number of mineral deposits around the world,

20 pyritic ores have a high carbon content and, when a high
level of carbon is present in the sulfidic material (eg.

2-20 wt% carbon), a surfactant such as a blinding agent is
preferably added to the solution during the contaminant
oxidation (leaching) step to prevent dissolved metals

25 (especially precious metals such as gold) from adsorbing
onto carbon in the material. The blinding agent is
typically one or more organic solvents including kerosene,
phenol ethers, etc.

Typically the contaminant oxidation (leaching) stage takes place at a temperature of around 100°C, which has been found to be an optimal temperature to achieve maximum leaching (oxidation) of contaminants such as arsenic, antimony etc.

In a second aspect, the present invention provides a .35 method of removing arsenic from a gold-bearing pyritic material comprising the steps of:

*leaching the material in a leaching stage wherein the material is mixed with an acidic aqueous metal chloride solution in which the metal has a relatively high oxidation state, such that the metal oxidises the arseni

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to render it soluble in the solution, produces a pyritic material refined of arsenic, and is reduced to a relatively lower oxidation state;

•precipitating and separating the arsenic from the solution
in a precipitation stage whilst simultaneously

- 10. regenerating the metal to its relatively high oxidation.
 - •returning the solution to the leaching stage with the metal in its relatively high oxidation state.

In a third aspect the present invention provides a

- method of treating a relatively high carbon content sulfidic material contaminated with a contaminant to allow recovery of a precious metal present with the material, comprising the steps of:
- Leaching the material in an aqueous solution wherein the
 contaminant and metal are solubilised in the solution,
 whilst masking the carbon in the material to prevent precious metal adsorption thereon; and
 recovering the precious metal from the solution.

When the term "relatively high carbon content" is 25 used herein it refers to a carbon content in the sulfidic material that is typically higher than about 2 wt%.

Preferably, the carbon is masked by adding a surfactant such as a blinding agent (as defined above) to the solution during leaching.

Typically the method of the second and third aspects is otherwise as conducted in the first aspect of the invention.

Brief Description of the Drawings

Notwithstanding any other forms which may fall within the scope of the present invention, preferred forms of the

invention will now be described, by way of example only with reference to the accompanying drawings in which Figure I schematically depicts a process flow diagram for a preferred method of removing a contaminant from a 5 sulfidic material, with associated recovery of precious metal from the sulfidic material; Figure-2 is-a Pourbaix diagram depicting various forms of the contaminant arsenic in solution at 25°C, and illustrating optimal process operating conditions.

Modes for Carrying out the Invention

Prior to describing preferred methods of the invention by way of example, a preferred method of the present invention will now be described in overview with 15 reference to Figures 1 and 2, with Figure 1 illustrating a typical process flow diagram.

Referring to Figure 1, a precious metal concentrate 10 for feeding to the process is prepared by mining, milling and then flotation of a sulfidic ore. Typically, the concentrate is a gold-containing arsenopyrite of highcarbon content (eg. 2 to 20 wt% carbon) . The concentrate is ground in a ball mill 12 and is then fed to a contaminant oxidation stage in the form of arsenic leaching stage 14.

25 Arsenic leaching may be conducted either in a single stage (eg. in a single processing unit, vessel or tank) or in a multi-stage process, typically a countercurrent leaching process (ie. having multiple units, vessels or tanks connected in a countercurrent configuration and 30 typically employing over and underflows (as is known).

In either case, in the leaching stage 14 a highly acidic environment is maintained (preferably less than ph I and as close to ph 0 as possible, as leaching of arsenic and gold etc from arsenopyrite is favoured by low solution 35 pH). The acid environment can be achieved simply by the oxidation of the sulfidic material (eg. where sulfur in the material is oxidised in solution to sulfate) or may

also require the addition of an oxidant (such as air, oxygen, chlorine, hydrogen peroxide etc) and/or a non-contaminating acid (such as sulfuric or hydrochloric acid). Also, in this regard, the solution Eh is typically maintained at greater than 0.4 volts (see Figure 2) to solubilise the contaminant and precious metal.

The solution is typically an aqueous cupric chloride

solution (typically having a chloride concentration of 7 moles/litre). In the leaching stage the cupric ion oxidises the sulfidic material to leach the arsenic, gold etc. into solution. At the same time, the cupric ion is reduced to cuprous ion. Thus, in the process, the copper acts as an electron transfer agent, but other agents can perform this function, including iron, cobalt, manganese, vanadium, etc.

Where the sulfidic material has a high carbon content

(eg. greater than 2 wt%) typically a masking surfactant is

added to the solution at stage 14 to prevent precious

metal adsorption onto carbon present in the material. The

20 surfactant is typically an organic blinding agent such as

kerosene, a phenol ether etc.

Reference is now made to Figure 2 which shows that at an acid pH less than 1, and at an Eh (oxidising potential) of from 0.4 to 1.25, arsenic is present in solution in the 25 soluble forms HAsO, or HaAsO. Thus, at a relatively modest oxidising potential and at a low pH, arsenic (and precious metal) can be readily leached into solution.

The arsenopyrite concentrate is leached for a predetermined period of time (see process examples described below) until a predetermined amount of arsenic has been leached out of the arsenopyrite material. For example, the amount may be determined by acceptable residual levels in the leached arsenopyrite material, assuming that it is to be separated and subsequently processed by conventional smelting or roasting techniques (described below). The term "refined arsenopyrite" or

"refined sulfidic material" is thus to be interpreted in this regard

In accordance with the invention, the solution ph an solution Eh are regulated such that the multi-valent species (eg. Cu(IT)) which oxidises the contaminant (eg. arsenic) from the material remains in solution and does not precipitate therefrom. In addition, the process operating conditions are controlled such that the contaminant (arsenic) and precious metal (gold) are

- 10 maintained in solution during a subsequent solid/liquid separation stage, which separates the refined arsenopyrite from the solution, prior to a subsequent arsenic precipitation stage.
- After leaching, the solution (leachate) is then
 15 passed to a thickening stage 16 wherein the solids
 (refined arsenopyrite) are flocculated (ie. by adding
 thereto a flocculating agent), with the solids dropping
 out as an underflow stream 18 and the pregnant supernatant
 solution passing out of the thickening stage as an
 - 20 overflow stream 20. The underflow or slurry 18 is then passed to a solid-liquid separation stage 22, where typically the solids are filtered thereat using a filtering apparatus.

The resulting liquid filtrate 24 is returned to 25 overflow stream 20, whereas the filtered solids (ie. refined arsenopyrite) 26 are passed to an optional conventional roasting stage 28 and conventional cyanide leaching stage 30, where a conventional gold product 32 can be produced. However, depending on the degree of

- 10 leaching of precious metal in arsenic leaching stage 14 the optional treatment may be rendered unnecessary or economically unfeasible, and hence the refined arsenopyrite may simply be disposed.
- A combined liquid stream 34, being the combination of streams 20 and 24, is then fed to a precious metal recovery stage 36. The recovery stage may comprise one or more columns filled with activated carbon through which

the solution is passed upwardly, such as in a fluidised bed arrangement. Dissolved gold (or other precious metal) in the solution adsorbs onto the carbon, whilst the dissolved arsenic in solution passes through the column as an overflow liquid stream 38. The activated carbon bearing gold is then removed periodically and passed as a gold product stream 40 (together with gold product stream 32) to a gold recovery process (eg. by burning or eluting

the carbon product).

dissolved arsenic) is passed to a contaminant precipitation stage in the form of arsenic precipitation stage in the form of arsenic precipitation stage 42. Stage 42 is typically operated at pH 2-3. In stage 42 an oxidant is introduced (eg. sparged) into the solution (eg. as air, oxygen, chlorine etc.) to raise the solution oxidising potential (Eh), causing the dissolved arsenic to assume one of its insoluble forms (typically iron arsenate FeAsO4 (scorodite), or where the contaminant includes antimony, iron antimonate). However, as the contaminant precipitate forms, an acid is typically generated. Thus, addition of an alkali may be required to consume acid and maintain optimum solution pH and Eh. Typically the alkali is an alkali salt such as calcium carbonate, calcium oxide etc.

25 Thus, in accordance with the invention the addition of oxidant and alkali is regulated to maintain optimum pH and Eh levels until all contaminant is precipitated, and to preferably then restore solution pH and Eh levels to those of the leaching stage 14, so that the soltuion can 30 then be recycled to that stage after contaminant precipitation.

Also, in accordance with the invention, the oxidant causes the cuprous copper to be oxidised to cupric copper, thus regenerating this species and allowing for its recycle and reuse. In other words, advantageously, the regulation of solution Eh and ph promotes the re-oxidation of the multi-valent species whilst maintaining it is

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solution at all times, so that, in the overall process, copper alternates between its +1 oxidation state and +2 oxidation state). In other words, the multi-valent species functions in the process as an electron transfer agent and 5 when the solution is recycled to the arsenic leach stage; the multi-valent species is ready to participate in further contaminant oxidation (leaching). This regeneration of the multi-valent species enhances the process economics, simplifies the process and completes to the process mass balance.

The solution from the arsenic precipitation stage including entrained arsenic precipitate, is then passed to a further thickening stage 44, to produce a solids (arsenic precipitate) underflow 46 that is passed to a 15 solid-liquid separation stage 48, and a supernatant liquid overflow stream 50 that is passed out of the top of the thickening stage. In the solid-liquid separation stage

48, typically the arsenic precipitate is filtered out using a filtration apparatus, producing a waste arsenic 20 product 52. The liquid filtrate is returned to the overflow stream 50 as liquid flow 54. The combined liquid stream 56 is then optionally passed to a further precious metal recovery stage 58, for example, an activated carbon column etc to recover any metal not recovered at stage 36.

The resultant precious metal and activated carbon stream 60 is combined with the other precious metal recovery streams 40 and 32, whilst a solution overflow 62 is recycled to the arsenic leaching stage 14 to close the process recovery loop.

Optionally, depending on whether or not there is contaminant build up in the overall process, a proportion of the recycle stream 62 may be recycled to a bleed circuit 64 to separate out any contaminant not recovered in the arsenic precipitation stage and optionally any other contaminants such as Mn, Cd, Ni, Co etc.

Now that the process has been described in overview, preferred examples of the method according to the present

invention will be described. In the following examples, an arsenopyrite concentrate from Bakyrchik, Kazakstan was processed. The aim was to develop a process that permitted processing of all samples of arsenopyrite ore provided 5 from the Bakyrchik mine.

Example 1

Concentrate Characterisation.

10 Method: 6kg of concentrate was processed by ultra fine regrinding. The concentrate possessed a Processed microns

Product	en la companya de la
Laser	Wt&
microns	passing.
20	100
18	99
15	96
	89
.10	81
1986 - 1986 - 1986 - 1986 1986 - 1986 - 1986 - 1986	69
6	50
·5·	42
3	15

The concentrate at P₁₀₀ 20 microns was received in three 15 cakes, the moisture content of each cake was determined, and the average was used as the moisture content for the concentrate.

Cake 1

20 Wet sample + paper: 113.84g

Dry sample + paper: 85.68g

Paper: 4.83g

Control of the Contro

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Dry sample: 80.85g

% Moisture: 25 8%

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Wet sample + paper Dry sample + paper: 66.65g Paper: 4.83g Dry sample: 62.02g % Moisture: 25% 9% ፡፡ Wet sample + paper: 86.41g 10 Dry sample + paper: 68.79g Paper: 4.85g

> The average moisture content determined was 24.4%. From this it was calculated that 100g of dry concentrate. translated to 132.3g of the wet concentrate sample.

Example 2

Dry sample: 63:94g % Moisture: 21.6%

Oxidation-Oxidation Leach Tests were then conducted to provide initial evidence of

arsenic leaching via a process of oxidation.

The Bakyrchik ore concentrate was noted to contain arsenic 25 as an arsenopyrite. The reaction was designed to determine if this arsenic could be rendered soluble (and hence be selectively removed) using cupric copper as oxidant

Method:

30 A 1L solution of 80g/L Cu²⁺ (as CuCl₂ 205.13g), 100g/L CaCl2, 200g/L NaCl and 30g/L NaBr was prepared, 140g of wet concentrate (-24% moisture, therefore 105.8g dry concentrate) was added to this the solution and the resultant slurry stirred at 105°C. The pH, Eh and Fe and Cu content were measured over the course of four hours

Solids were subsequently filtered using a Buckner apparatus and the filtrate preserved for further analysis.

Solid cake was washed with low pH brine (~0.5L, 280g/L, pH 0.3), the resultant moist cake was weighed, dried in an 5 oven and weighed again. The dry solids were preserved for further analysis.

Results and Discussion:

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10 The pH, Eh and Fe and Cu tenor recorded over time were summarised as per the table below.

TIME (MIN)	pH	Eh (mV)	Fe (g/L)	Cutot (g/L)
One of the second second second second	At the sound of the sound	and the second second second	*** **** *** *** *** ** *** *** *** **	See St. Albertage v.
30.	1.45	740	2.4	70.6
60 · · · · · · · · · · · · · · · · · · ·	0.5	508	· 2 E · · · · · · · · · · · ·	
90	1.0.5	*507* **** ***	A A A A ANSON ALL	**
1,50	11 14 40 - 12 12 1 1 W 11 1 1 1 1 1 1 1 1 1 1 1 1	495	2 65	AZXIVI MOVIDI IX
	LUMBAR	ברם בייי	T	
70	0.35	4.95	2.68	
	00	4.05		65

Wet cake + paper + filter paper: 168.2g

15 Dry cake + paper + filter paper: 99.96g

Paper + filter paper: 11.74g

Dry cake obtained: 88.2g

Moisture component: 68.24g (43.6%)

The reaction appeared to proceed quickly. A significant drop in Eh and, to a lesser extent, pH was observed within the first hour of the reaction's progress. After this time the reaction stabilised and did not appear to progress further

The total mass of the solids retrieved from the solution was significantly less than the mass of the solids fed to the solution. The increase of the iron tenor of the

solution along with the reduction in the mass of the solids present suggested that iron was being leached from the feed. An analysis of the arsenic content of both the feed and solid residue was then required to determine

Example 3

Oxidation Leach

The aim of this example was to investigate whether fresh10 liquor would facilitate the further leaching of the iron/
arsenic from the previously leached material. It was
surmised that treatment of the solid obtained from the
previous leach would remove more of the arseno-pyrite. A
fresh solution of the primary liquor was prepared and a
repeat of the previous leach was performed using the
leached material as the solid feed.

Method:

A 500ml solution of 80g/L Cu²⁺ (as CuCl₂ 102.55g), 100g/L

20 CaCl₂, 200g/L NaCl and 30g/L NaBr was prepared. 30g of the
leached concentrate obtained from the previous oxidation
was added to this the solution and the resultant slurry
stirred at 105°C. pH and Eh were measured over the course
of four hours. Solids were subsequently filtered using a

25 Buckner apparatus and the filtrate preserved for further
analysis. Solid cake was washed with low pH brine (-0.5L),
280g/L, pH 0.3), the resultant moist cake was weighed,
dried in an oven and weighed again. The dry solids were
preserved for further analysis.

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Samples taken from the solids obtained from this and the previous reaction as well as the original concentrate were digested using Aqua-regia/perchloric acid. These solutions were then analysed for Arsenic using ICP.

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GRIFFITH HACK

The pH, Eh recorded over time were summarised as per the

Time ... Eb (mv) (min) 1.2 615 30 0.55 588 60 0.31 583 580 0.29 120 579 ·150 0.31 569 **180**.... 0.300.000 574.... 210 574

1--03 TUE-18:11 FAX 61299255911-

Wet cake + paper + filter paper: 72.5g
Dry cake + paper + filter paper: 40.24g
Paper + filter paper: 11.5g
Dry cake obtained: 28.74g
Moisture component: 32.26g (52.9%)

The ICP analysis for Arsenic in the recovered solids were summarised as per the table below.

Sample	As (%)
Bakyrchik concentrate	34.0
2 201 - 3 200 - 11 1 A 200 - 10 10 10 10 10 10 10 10 10 10 10 10 10	*** *** * **** *** ***
Leach 1	7 70
The second secon	And the second of the second o
Leach 2	D 70

As was observed in the previous leach the reaction appeared to proceed quickly, stabilising over the course of an hour. A significant drop in Eh and, to a lesser

extent, pH was again observed along with a decrease in the same of the solids recovered when compared to the mass of the solids fed to the solution. This suggested that there was material left in the residue from the primary leach that was still extractable. An analysis of the arsenic content of both the feed and solid residue from both

leaches revealed a progressive reduction in the arsenic content of the solids recovered. The results suggested that the method could be refined to selectively leach the arsenic contained within the Bakyrchik concentrates.

15 Example 4

****Oxidation Leach

The aim of this example was to refine the conditions used in leaching arsenic from the Bakyrchik ore. Having succeeded in leaching -65% of the arsenic contained within 20 the Bakyrchik ore, the method was refined to obtain a greater leach performance. The method focused on two areas: firstly the leach liquor was simplified, and secondly, the reaction was carried out at various temperatures and starting ph's to determine the effect these changes had on improving the leach efficiency.

Method:

A 5L solution of 80g/L Cu²⁺ (as CuCl₂ 1025.64g), 150g/L CaCl₂ (750g) and 150g/L NaCl (750g) was prepared and heated to 80°C. This solution was then divided into three 1.5L solutions, each solution performing an oxidation leach under different conditions on the equivalent of 142.86g wer concentrate (-24% moisture, therefore 108g dry concentrate).

Oxidation Leach Solution 1: Leach was performed at 80°C

Oxidation Leach Solution 2 - Leach was performed at 100 c

Oxidation Leach Solution 3: Leach was performed at 80°C.

Starting pH <0.4, Eh >550mV

The pH and Eh of these solutions was measured over the course of two and a half hours. Samples from each were taken at intervals and analysed for their iron and copper content.

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Solids were subsequently filtered using a Buckner apparatus and the filtrate preserved for further analysis.

Solid cake was washed with low pH brine (~1L, 280g/L, pH 0.3), and the resultant moist cake was weighed dried in an oven and weighed again. The dry solids were preserved for further analysis.

Samples taken from the solids obtained from each reaction as well as the original concentrate were digested, one set using Aqua-regia/perchloric acid (HS and PM), the second using a 1:1 solution water/concentrated hydrochloric acid (HCL). These solutions were then analysed for arsenic, copper and iron using ICP.

Results and Discussion:

Oxidation Leach Solution 1 (80°C)

·	J	f		Fe	1 430 V LODMI	Commente
(min)	A		(g/L)	(g/L	From ICP	
0×4×4 · · · · ·			and many or .			Solids added
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30.	0.95	535		0.79	824	
The or amountaining	7. *********	20200	- 1 Jac 18 18 1 Ja	Transfer with	-±U⊙⊙	
2000 000000 0000 000 000 00	11111 VAL 2	13 3 3 4 20 10 10 10 1	7.5	1720	~T-T-T-D-T	Anna Anna Anna Anna Anna Anna Anna Anna

Dry cake + paper + filter paper: 105.48g

5 Dry cake obtained: 93.98g Moisture component: g (39.7%)

Committee of the contraction			80 - 1000 f 100 million	Market A. Lettersteiness	·3000/3000000 / 0 /	er tekster og som er sterender i sen er	nn an taran an a
			Eh	Cu	Pe	As (ppm)	Comments
control and self-responding to the self-re-	(min)		(mV)	(g/L)	(g/L	From ICP	
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Wasterman	60	1.05	528			1473 1532	The state of the s
200 Material Control of the Control	.90	0.98		66	2.0	.1636	Miles and the second of the second second of the second second of the second se
make the second of the second	.120	0.94		.84 :	2.0	1678	
2000 - 10	.150	0.89	528	·85·····	2.14	-1.0 C1. I	e de la composició de l
30.17.0.201			A MARKET	the water of the same	'You		· · · · · · · · · · · · · · · · · · ·

Wet Cake '+ paper '+ filter paper: 170.3g Dry cake + paper + filter paper: 113.32g Paper + filter paper: 11.5g

15 Moisture components 56.98g (35.88 %).

Oxidation Leach Solution 3 (80°C, low pH)

Time	рн	Eh	Cu	Fe	As (ppm)	*Comments
(min)		(mV)	(g/L)	(g/L	From ICP	
tiona a manazi.	-0.00 -0.00		to Administration of the)		
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70	0.5	525	74	1.51	1082	energe error, and a service error of the

120 0.4 520 75 1.61 1162 150 0.43 515 73 1.61 1181

Wet cake + paper + filter paper: 172.4g Dry cake + paper + filter paper: 108.46g Paper + filter paper: 11.5g

5 Dry cake obtained: 96.96g

Moisture component: 63.94g (39.7%)

The ICP analysis for arsenic in the recovered solids were summarised as per the table below.

10.

W 255 (5.5)			and well and a second
		*Cus	Fe%
	3.22		
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HS 3	1.59	.0.32	5.56
PM. I. w	1.05	0.3	
PM 2	0.26		2.82
	1.55		
Martinian and the contract of	0.083	0.177	
HCL 2	1 .	0.229	.VV
HCL 3	And the property of the second	Suppose a visit of the second	0.63
A CONTRACTOR OF THE CONTRACTOR	Committee of the Commit	* **********	.0.03

HS Samples fall into analytical range of ICP method

PM Samples were over-range

15 Example 5

Oxidation Leach

Method:

A 12L solution of 80g/L Cu²⁺ (as CuCl₂ 2461.5g), 150g/L CaCl₂ (1800g) and 150g/L NaCl (1800g) was prepared and 20 heated to 105°C. 1680g wet concentrate (~24% moisture, therefore 1270g dry concentrate or 105.8g/L) was added to this the solution and the resultant slurry stirred at 105°C. The pH and Eh of the solution were measured over the course of seven hours.

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.5	2.0	1.6	555	0.83	86	1.12	The second	85	0.94	
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8	50	1.2	535	1.43	8.7	1.96	* * ·	87	1.76	
~ <u>*9</u>	60	1.2	535	1.33	87	1.8	- 	86	1.6	560g cons
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Example 6

Iron/Arsenic Rejection process
Method:

Liquor obtained from the oxidation reaction (101) was
returned to the vat and heated to 80°C with low stirring.

10 Upon reaching this temperature the pH and Eh of the Liquor were measured and a sample taken. The liquor was then aerated (100L/Hr) with agitation, and the pH and Eh of the liquor was measured and a sample was taken every thirty minutes thereafter. After four hours the rejection process was considered to be complete; the liquor was filtered using a Bucher apparatus and the rejected iron precipitate was removed as a filter cake. The wet cake was weighed, and then dried over twenty-four hours in an oven. The dry cake was then weighed and a sample digested for analysis

Results and Discussion:

The pH and Eh and tenor of the liquor over time were summarised as per the table below.

Ø1007

Time ρĦ Eh. Sampl BAA AAS Comments mins (mV) e No. (g/L) (g/L) Cu Fe : (g/L) (g/L) 0.7 500 2.8 3.7.... 88... 3.7. Vol.:10L 0 0.7 500 C air@l00L/Hr 1.1 510 2.3 3.6 90 1.5 520 2.7... 2.6 9D... 1.6 525 0.6... 2.4 91 120 ... 2.0. 530 5.... 0.3 85... 1.6 150. 2.10 535 180 2.1 545 210 555 240 2.5 570 ND: 880 <0.1. Cutot 88, Cu2+:88

Wet cake + paper + filter paper: 257.2g

Dry cake + paper + filter paper: 128.94g

Paper + filter paper: 11.5g

5 Dry cake obtained: 117.44g

Moisture component: 128.26g (47.8%)

Example 7

10

Leach on regenerated liquor, lower slurry density Method:

A 90g sample of wet concentrate (-24% moisture; therefore
5 68g dry concentrate) was added to the liquor obtained from
the oxidation reaction (1.5L) and the resultant slurry
stirred at 100-105°C. The pH and Eh of the liquor were
monitored and a sample taken every thirty minutes over a
four hour period. After this period the liquor was
filtered using a Bucher apparatus and the filter cake
removed, the wet cake was weighed and then dried over

-- 26

twenty-four hours in an oven. The dry cake was then weighed and a sample digested for analysis.

Results and Discussion:

5 The pH and Eh and tenor of the liquor over time is summarised in the table below.

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10 Dry cake obtained: 58g

Now that preferred operating details of the process have been exemplified, it will be appreciated by those skilled in the art that the method of the present invention includes the following advantages:

- 15 The method can be employed to recover precious metals from sulfidic ores and concentrates which are otherwise difficult or impossible to treat using conventional available processes/techniques such as smelting and roasting.
- 20. The method can accommodate a high carbon content in such ores, because the method is conducted in solution, and thus blinding agents can be employed to prevent precious metal adsorption onto carbon, which can otherwise interfere with precious metal recovery.

e allegation in Continuents Water and in the information The method can be employed to remove contaminants from wide variety of ore and concentrate feedstocks which, onc removed, can then be treated using conventional smelting/roasting techniques. 5 • The method has the capacity to recover a wide variety of metals of economic value, especially precious metals, using simple non-cyanide based leaching and separation processes, and including activated carbon adsorption. • The method can be used to treat contaminated residues to 10 allow them to be subsequently disposed of with reduced ...environmental impact. Whilst the invention has been described with * reference to a number of preferred embodiments it should be appreciated that the invention can be embodied in many 15 other forms.

CLAIMS

- 1. A method of removing a contaminant from a sulfidic material comprising the steps of:
- •mixing the material in an aqueous solution wherein a multi-valent species of a relatively high oxidation state oxidises the contaminant to render it soluble in the solution, produces a contaminant refined material, and is reduced to a relatively lower oxidation state; and
- **precipitating the contaminant from the solution whilst

 10 regenerating the multi-valent species to its relatively

 high oxidation state.
 - 2. A method as claimed in claim 1 wherein the multivalent species oxidises the contaminant in a leaching stage, and the contaminant is precipitated from the
- 15 solution in a precipitation stage through the introduction of an oxidant which simultaneously causes the multi-valent species to be oxidised to its relatively high oxidation state.
 - 3. A method as claimed in claim 2 wherein, after precipitating and removing the contaminant and regenerating the multi-valent species to its higher oxidation state, the solution is recycled to the leaching stage.
 - 4. A method as claimed in claim 3 wherein in the precipitation stage the solution photos maintained at around ph 2-3.
 - 5. A method as claimed in claim 4 wherein the solution pH is maintained by regulating the supply to the solution of the oxidant and/or an alkali agent.
- 30. 6. A method as claimed in any one of the preceding claims wherein the sulfidic material includes, in addition to the contaminant, a metal to be recovered, the method further comprising a metal recovery stage intermediate contaminant oxidation and precipitation.
- 35 7. A method as claimed in claim 6 wherein the metal is a precious metal such as gold, silver, platinum or other platinum group metal.

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8. A method as claimed in claim 6 or 7 wherein in the metal recovery stage the metal is adsorbed onto carbon such as activated carbon.

- 9. A method as claimed in any one of claims 6 to 8
 further comprising a material separation stage,
 intermediate contaminant oxidation and metal recovery, to
 remove the refined material from solution prior to metal
 recovery.
 - 10. A method as claimed in claim 9 further comprising a thickening stage, after contaminant oxidation and prior to the material separation stage, to thicken the refined material to render it easier to separate from the solution.
- 11. A method as claimed in claim 9 or 10 wherein the material separation stage involves filtering the refined material from the solution.
- 12. A method as claimed in any one of claims 9 to 11 further comprising a material treatment stage, after material separation, to further treat the separated 20 refined material to recover any metal remaining therein.
 - 13. A method as claimed in claim 12 wherein in the material treatment stage the separated refined material is roasted and then leached with a cyanide containing solution to recover any remaining metal therein.
 - 14. A method as claimed in any one of claims 6 to 13 which, after contaminant precipitation, further comprises a contaminant separation stage to remove the contaminant from solution prior to further metal recovery, or prior to recycling the solution to the material mixing stage.
- 30. 15. A method as claimed in claim 14 further comprising a thickening stage, after contaminant precipitation and prior to the contaminant separation stage, to thicken the contaminant to render it easier to separate.
 - 16. A method as claimed in claims 14 or 15 wherein the contaminant separation stage involves filtering the material from the solution.

- 17. A method as claimed in any one of the preceding claims wherein the contaminant is oxidised in a highly acidic aqueous solution of pH less than 1.
- 18. A method as claimed in claim 17 wherein the solution
 5 pH is further maintained by adding thereto an acid such as sulphuric acid or hydrochloric acid.
 - 19. A method as claimed in claim 17 or 18 wherein an oxidant such as air, oxygen, chlorine gas or hydrogen peroxide is added during the contaminant oxidation step.
 - 10 20. A method as claimed in any one of the preceding claims wherein the aqueous solution includes a dissolved metal chloride.
 - 21. A method as claimed in claim 20 wherein the chloride concentration is approximately 7 moles/litre.
 - 15 22. A method as claimed in claim 20 or 21 wherein the metal in the dissolved metal chloride functions as the multi-valent species.
 - 23. A method as claimed in claim 22 wherein the metal in the metal chloride is copper or iron.
 - 20 24. A method as claimed in claim 23 wherein in the higher oxidation state the metal is Cu(II) or Fe (III) and in the lower oxidation state the metal is Cu(I) or Fe (II).
 - 25. A method as claimed in any one of the preceding claims wherein the sulfidic material is a pyritic ore or 25 concentrate.
 - 26. A method as claimed in any one of the preceding claims wherein the contaminant is arsenic; antimony or bismuth present in the sulfidic material.
 - 27. A method as claimed in any one of the preceding
 - 30 Claims wherein the sulfidic material includes a high level of carbon, and a surfactant is added to the solution during the contaminant exidation step to prevent dissolved metal from adsorbing onto the carbon.
 - 28. A method as claimed in claim 27 wherein the
 - 35 surfactant is a blinding agent such as one or more organic solvents including kerosene or a phenol ether.

9. A method as claimed in any one of the preceding ...claims..wherein..during..contaminant..oxidation..the..soluti temperature is maintained at about 100 degrees C. -30. A method of removing arsenic from a gold-bearing pyritic material comprising the steps of: •leaching the material in a leaching stage wherein the material is mixed with an acidic aqueous metal chloride solution in which the metal has a relatively high oxidation state, such that the metal oxidises the arsenic -10 --- to render it soluble in the solution, produces a pyritic material refined of arsenic, and is reduced to a relatively lower oxidation state; precipitating and separating the arsenic from the solution in a precipitation stage whilst simultaneously 15 regenerating the metal to its relatively high oxidation state; and •returning the solution to the leaching stage with metal in its relatively high oxidation state: 31. A method of treating a relatively high carbon content sulfidic material contaminated with a contaminant to allow recovery of a precious metal present with the material, comprising the steps of: •leaching the material in an aqueous solution wherein the contaminant and metal are solubilised in the solution, whilst masking the carbon in the material to prevent precious metal adsorption thereon; and •recovering the precious metal from the solution. 32. A method as claimed in claim 31 wherein the carbon is masked by adding a surfactant to the solution during

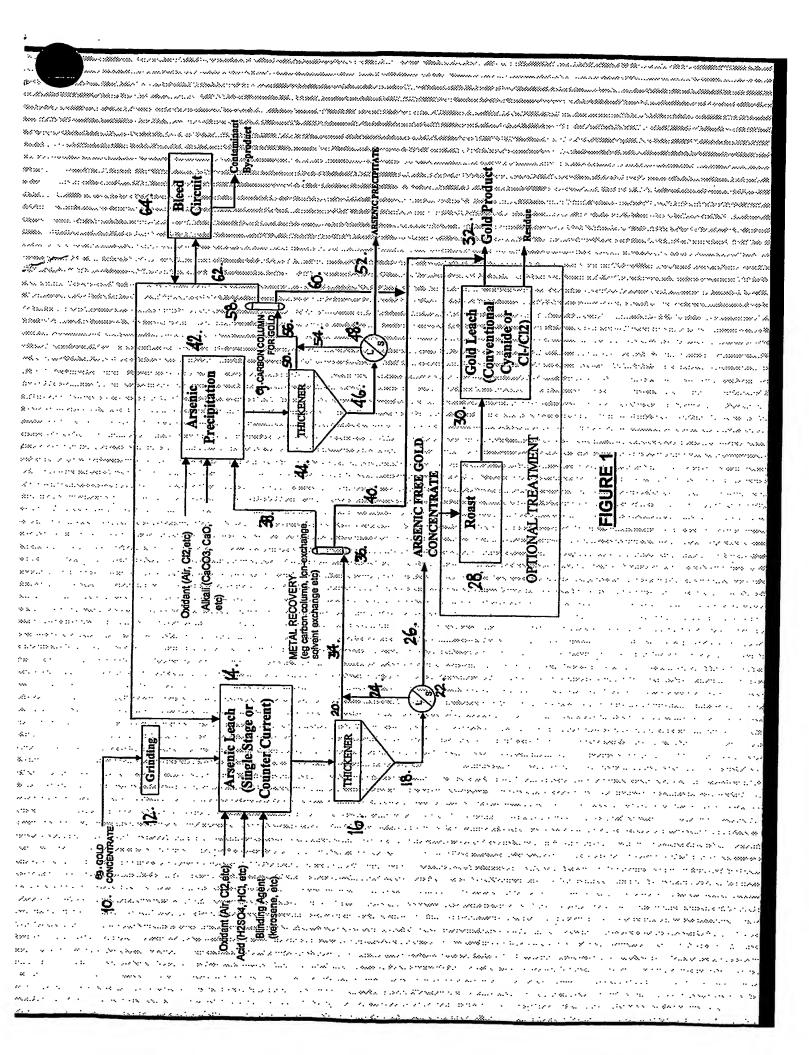
33. A method as claimed in claim 32 wherein the surface is a blinding agent as defined in claim 28.

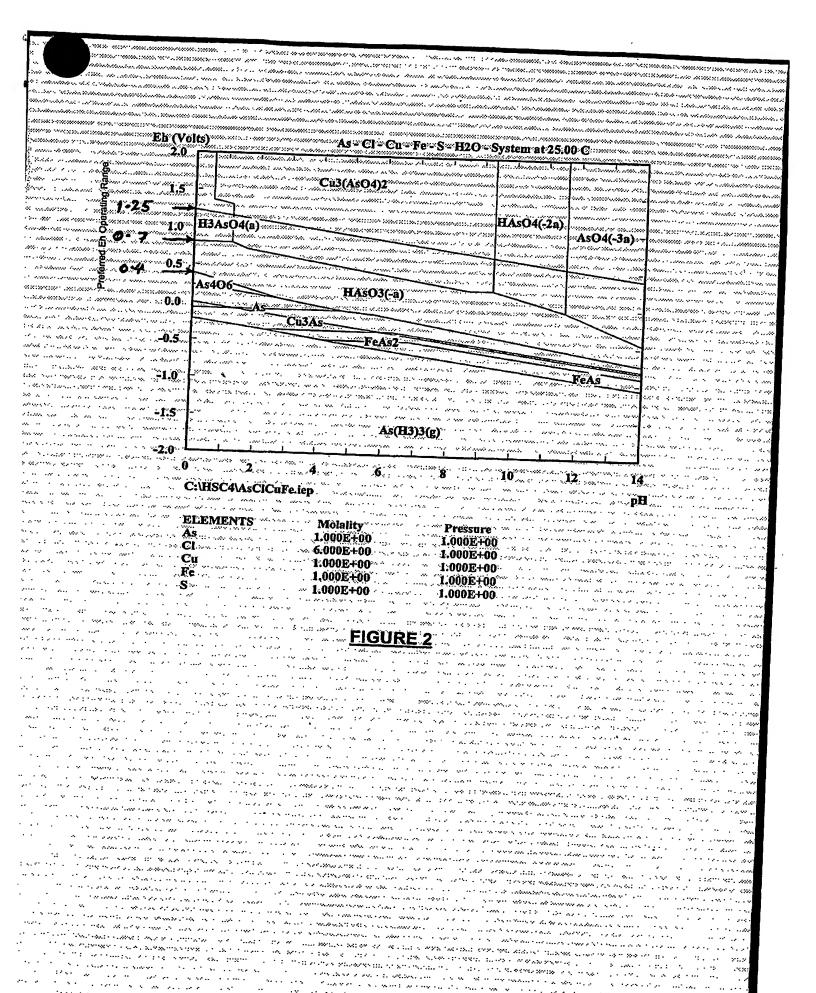
34. A method as claimed in claim 30 or 31 which is otherwise as defined in any one of claims 2 to 29

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